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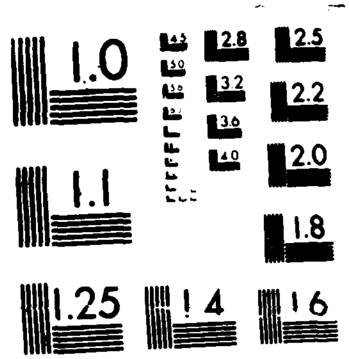

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The syntheses of a large number of stable compounds which contain difluoroaminoxy (ONF_2) difluoroamino (NF_2), nitroso (NO), nitro (NO_2), azo (-N=N-), fluorimino (=NF), and/or dichloroamino (NCl_2) groups have been accomplished successfully. The mechanisms for their formation have been elucidated and their reaction chemistries studied extensively. In many cases their structures have been determined through the use of electron diffraction or X-ray crystallographic techniques. It has been found that NF_3O is a powerful precursor for NF_2O-containing compounds as well as for the in situ preparation of FNO when reacted with NO. Fluorination of NOCl or NO_2 with KF also provides a ready source of FNO which has served as a useful precursor for a number of F-nitroso compounds whose chemistry has been pursued additionally. Tetrafluorohydrazine with polyfluoroolefins provided intermediates which led to new families of mono and bis dichloroamines that could be converted easily to highly fluorinated diazines. In addition, new highly substituted fluoroethers have resulted from reactions of perfluoroalkyl hypochlorites. These stable fluids have (over)

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19. continued

approximately the same polar character but are significantly more stable both thermally and hydrolytically than the chloro analogues. Other hydrolytically and thermally stable fluids have resulted from the reactions of substances formed when perfluoroalkyl sulfites undergo surprising Arbuzov rearrangements to give fluorosulfates. The latter give fluids with polyfluoroalcohols or primary amines which are resistant to nucleophilic attack. Studies of tetrafluorothane-ß-sultone with nucleophiles have led via a multi-step process to new families of esters, ethers and finally polyfluoroalkyl sulfonic acids which are highly acidic but water and heat insensitive. Additionally, analogous families of polyfluoroalkylphosphonic and phosphinic acids have been synthesized. Reactions of the latter with chlorine fluoride give the first examples of fluoroalkyl phosphorus(V) peroxides and hypochlorites. Carbonyl fluoride has been demonstrated to be an extremely versatile mild fluorinating agent which is very useful for replacing C-H, P-H, N-H, M-O (M = metal) bonds with C-F, P-F, N-F, M-F, respectively, and for oxidative addition fluorination reactions.

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Final Report

AFOSR 82-0247
September 1, 1982-November 30, 1986

Synthesis of Difluoroaminoxy-, Difluoroamino- or Fluorodiazonium-Containing Materials

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I. Summary of Research (AFOSR 82-0247)

During the period covered by this report (September 1, 1982-November 30, 1986), the following progress was made.

A. Compounds that contain NF_2O, NO, NO_2, =NF, -N=N-, NCl_2 or NF_2 functionalities

Although NF_3O is kinetically inert, it can be reacted with strong Lewis acids either at ambient or lower temperature to form a white salt, e.g., with AsF_5 to form $NF_2O^+AsF_6^-$ which is partially dissociated to the reactants at 25 °C. When a trifluorovinyl olefin was added to the salt in the presence of excess NF_3O, the corresponding N,N-hydroxylamine results. With totally fluorinated 1-alkylolefins (C_3F_6 and C_7F_{14}) or with other trifluorovinyl olefins (CF_2=$CFSF_5$ and CF_2=CFC(O)F) only Markovnikov-type addition was observed, i.e., F added to the vinyl methylene carbon. However, for olefins F_2C=CFR_f (R_f = OC_2F_5, $OCF_2CF(CF_3)OC_3F_7$, Cl or Br) only anti-Markovnikov-type addition occurred, e.g., NF_2O added to the vinyl methylene carbon. To test the relationship between orientation of addition and the presence of an atom in the vinylic position to donate electrons, NF_3O was added to the pentafluoroalkylic ethers CF_2=$CFCF_2OCF_2CF(SO_2F)CF_3$ and CF_2=$CFCF_2O\overline{CFOCF(CF_3)CF_2OC}F(CF_3)$ to give exclusively the Markovnikov-type addition products. We believe the orientation of addition can be explained by electrophilic attack of NF_2O^+ on the double bonds: perfluoroalkenes gave Markovnikov products while perfluorovinyl ethers yielded products with the opposite orientation due to the reversed polarity of the double bond. Addition reactions occur with terminal olefins only. The compounds formed in the reaction are colorless, thermally stable liquids.[1]

During the investigation of trifluoramine oxide addition to fluoroolefins, the occasional formation of small amounts of intensely blue nitroso compounds, particularly at elevated temperatures, was observed. For example, in an effort to form $(CF_3)R_fCFONF_2$, via a thermally-induced, free radical addition of NF_3O to a fluoroolefin, only perfluoronitrosoalkanes and perfluoroalkanes were observed. This probably occurs via a free radical abstraction of fluorine from NF_3O by the olefin to form the alkane and to produce ONF which subsequently adds to the olefin.

Taking advantage of the ability of radicals to abstract F· from NF_3O, it was found that when two parts NO and three parts NF_3O were reacted with three parts olefin, e.g., F_2C=$CF(n\text{-}C_5F_{11})$ in the presence of KF with acetonitrile as solvent, a 78% yield of the nitroso compound resulted. This method was also useful in converting CF_2=$CFSF_5$ and CF_2=$CFOC_2F_5$ to their respective deep blue nitrosos in good yield. Only Markovnikov-type addition occurred.[5]

In continuing the studies of the synthesis of nitroso-containing compounds, hepatafluoronitrosocyclobutane and nonafluoronitrosocyclopentane were prepared via reaction of the perfluorocycloolefin with ONF which was generated *in situ* from ClNO or NO_2 with KF in acetonitrile. The formation of the nitroso compounds is believed to be a stepwise process with the ClNO (NO_2) initially and rapidly being converted to ONF followed by its much slower addition to the olefin. The cyclic nitroso compounds underwent thermal decomposition at 165 °C in Pyrex glass to form colorless nitro derivatives. 1,2-Cycloaddition reactions occur with C_2F_4 to give oxazetidines, and 1,4-cycloaddition reactions with 1,3-hexafluorobutadiene gave oxazines. When the

nitroso compounds are heated with N_2F_4 in the presence of SiO_2, perfluorocycloalkyl-N'-fluorodiimide N-oxides, e.g., $\boxed{F}N(O){=}NF$, resulted. However, in the absence of glass, (perfluorocycloalkyl)difluoroamines, e.g., $\boxed{F}NF_2$, formed. All of the new compounds are stable at 25 °C and are hydrolytically stable, at least in the presence of moist air. A molecular ion was observed in the mass spectra of all of the perfluorocyclicalkylnitroso derivatives.[3]

Further studies on the reaction chemistry of $c\text{-}C_4F_7NO$ and $c\text{-}C_5F_9NO$ with aromatic amines in methanol gave rise to a new family of stable perfluorocycloalkyl(aryl)diazenes. These are bright yellow materials that were prepared in low yield and were difficult to purify.[7] It is interesting to note that when CF_3NO was reacted with CH_3NH_2, $CF_3N{=}NCH_3$ was produced whereas when $\overline{CF_2(CF_2)_2C}FNO$ was reacted similarly with CH_3NH_2, a diazene 1-oxide $CH_3N(H)\overline{CCF_2CF_2C}N(O){=}NCH_3$ formed. This was confirmed by an X-ray crystal structure determination.[8]

A gas phase electron diffraction structure determination was done for $c\text{-}C_4F_7NO$. Comparison with the parent compound, C_4H_8, demonstrates that fluorination of the ring results in lengthening the C-C bonds and flattening of the ring. Just as for CF_3NO, the C-N bond is longer than expected for a $N(sp^2)\text{-}C(sp^3)$ bond. The exo orientation of the NO group, i.e., eclipsed position with respect to the geminal F atom, corresponds to the eclipsed conformation observed for CF_3NO.[9]

Some very interesting new N,N-dichloro, N,N-difluoro and -N=N-compounds resulted from the reactions of chlorine fluoride with polycyano compounds or with difluoroamino or fluoroimino nitriles. For example, with tetracyanoethers and chlorine fluoride, saturation of triple bonds occurred with concomitant loss of $[NCl_3]$ to leave a five-membered unsaturated heterocycle, $Cl_2NCF_2\overline{C{=}C(CF_2NCl_2)CF_2N(Cl)C}F_2$, and with KCN, chlorine fluoride gave $FC(CF_2NCl_2)_3$.[28]

The reactions of olefins $R_fR_f'C{=}CH_2$ ($R_f = R_f' = F$; $R_f = F$, $R_f' = H$; $R_f = CF_3$, $R_f' = H$) with N_2F_4 gave NF_2CF_2CN and $R_fC(CN){=}NF$ ($R_f = F$ or CF_3) that when reacted with chlorine fluoride gave stable N,N-dichloroamines, or in the case of the latter compound N,N-dichloroamine or N,N-dichloroamine-N',N'-chlorofluoroamine. After complete characterization, photolysis of $-NCl_2$ compounds gave rise to a new family of stable diazenes.[21] The study of the reactivity of NF_2CF_2CN was extended to include its behavior with NH_3, NH_2OH, $N_2H_4{\cdot}HCl$, and a variety of polyfluoroalcohols and diols. When the product from the ammonia reaction was thermolyzed at 135 °C, a stable heterocycle, $NF_2CF_2\overline{C{=}N\text{-}C(CF_2NF_2){=}NC(NH_2){=}N}$, formed. With $CF_3C({=}NF)CN$, ammonia gave three products that exist in equilibrium at 25 °C $H_2N\overline{C{=}N\text{-}N{=}C}(CF_3) \rightleftharpoons HN{=}\overline{CNHN{=}C}(CF_3) \rightleftharpoons HN{=}\overline{CN{=}NC}H(CF_3)$.[27]

The study of $-NF_2-$ and $=NF$-containing compounds continues. Interest is still high in obtaining $R_fN{=}NF$, $R_fN{=}NR_f'$ and other reactive difluoroamino compounds.

B. Reactions of trifluoromethyl or of perfluoro-t-butyl hypochlorites

Trifluoromethyl hypochlorite has been reacted with $RCH{=}CH$ ($R = SO_2CH{=}CH_2$, $(CH_3O)_3Si$, Cl_3Si, $(CH_3)_3Si$) to form isomeric mixtures of the trifluoromethyl ethers. With SbF_3, $CF_3OCH_2CH(SiCl_3)Cl$ gave $CF_3OCH_2CH(SiF_3)Cl$, and when $CF_3OCH[Si(CH_3)_3]CH_2Cl$ was thermolyzed, the vinyl ether $CF_3OCH{=}CH_2$ resulted.

The addition product of CF_3OCl with $Cl_2C{=}CHCl$ was dehydrochlorinated to $CF_3OCCl{=}CCl_2$, which when chlorinated gave $CF_3OCCl_2CCl_3$. The latter could not be obtained by direct reaction of CF_3OCl with tetrachloroethylene. Dechlorination of the $CF_3OCl/Cl_2C{=}CF_2$ addition product gave $CF_3OCCl{=}CF_2$, which formed a bis(trifluoromethyl)ether, $CF_3OC(Cl)OCF_3CF_2Cl$ that could be dechlorinated with Φ_3P to form $(CF_3O)_2C{=}CF_2$. 1,1,1-Trifluoropropene with CF_3OCl gave a 60% yield of the Markovnikov-type addition product, $CF_3OCH(CF_3)CH_2Cl$, which when reacted with KOH formed cis-$CF_3CH{=}CClH$ as a result of $[CF_3OH]$. The yields of trifluoromethyl ethers formed by reaction of $CH_3OC(O)CH{=}CH_2$, $CH_3C(O)CH{=}CH_2$, and $HC(O)CH{=}CH_2$ with CF_3OCl decreased from 65 to 5%.[12]

The reactions of CF_3OCl with $SF_5CF{=}CF_2$, $SF_5CCl{=}CH_2$, $SF_5CH{=}CF_2$, $CF_3SF_4CF{=}CF_2$ also gave isomeric mixtures of the addition products with the first olefin, but for the latter three the major products resulted from the addition of ClF not CF_3OCl. A rationale for the differing behavior of CF_3OCl with olefins based on the relative electronegativities of the substituent groups was proposed.[19]

Although not as thermally stable as CF_3OCl, $(CF_3)_3COCl$ shows a much more interesting and varied collection of behavioral modes including its oxidative addition to elements or to central atoms in molecules where their oxidation state is not maximum. Thus, we have shown that it will add to a variety of iodo-compounds at 0 °C. For example, with CF_3I, ICF_2CF_2I, $SF_5CF_2CF_2I$ and C_6F_5I, the following I (III) compounds, $CF_3I(OR_f)_2$, $(R_fO)_2ICF_2CF_2I(OR_f)_2$, $SF_5CF_2CF_2I(OR_f)_2$ and $C_6F_5I(OR_f)_2$ ($R_fO = (CF_3)_3CO$), resulted, respectively. In addition, with $C_6F_5I(OR_f)_2$, further addition to the ring occurred, $(R_fO)_2IC_6F_5(R_fO)_2Cl_2$. No I (V) compounds resulted regardless of conditions employed.[14]

C. Formation of polyfluoroalkyl fluorosulfates and their reactions with selected nucleophiles

In a very unexpected reaction, we found that polyfluorinated alkyl sulfites undergo an Arbuzov rearrangement with ClF - a rare mode of reaction for sulfur compounds.[4] Xenon difluoride as the fluorinating agent gave the same products although in lower yields. Polyfluoroalkyl fluorosulfates, R_fOSO_2F [$R_f = CF_3CH_2$, $(CF_3)_2CH$, $CF_3(CH_3)_2C$, $CF_3CH(CH_3)$, CH_3CH_2], which resulted from the Arbuzov rearranged product of ClF + $(R_fO)_2SO$, were formed in higher yields than from reaction of the respective polyfluoro alcohol with sulfuryl fluoride or sulfuryl chloride fluoride. When reacted with amines and alcohols or alkoxides, new polyfluoroalkyl sulfamates and dialkyl sulfate esters formed. Unlike both perfluoroalkyl fluorosulfates and alkyl fluorosulfates, the sulfur-oxygen bond in these polyfluoroalkyl fluorosulfates remained intact in the presence of hard nucleophiles. With methanethiol and bromide ion, however, nucleophilic attack occurred primarily at the α-carbon of $CF_3CH_2OSO_2F$ to give methyl 2,2,2-trifluoroethyl sulfide and 2,2,2-trifluoroethyl bromide, respectively. In sharp contrast fluoride ion was inert toward these materials. Unlike perfluoroalkylfluoro- and chlorosulfates, the fluorosulfates in this study were remarkably stable to hydrolysis. In addition the sulfamates were colorless, air and water stable liquids or solids with very low vapor pressures. All of the dialkyl sulfate esters are involatile liquids, insensitive to both air and water.[6,11]

D. Synthesis of polyfluoroalkyl esters of difluoro(fluorosulfonyl)acetic acid, diesters of difluoro(sulfonyl)acetic acid and some electron diffraction structural studies of cyclic tetrafluorosulfur(VI) compounds

Tetrafluoroethane-β-sultone is a vulnerable target for a variety of nucleophilic reagents, such as amines, mercaptans, alcohols, hydrogen sulfide and carboxylic acids. Advantage has now been taken of the electrophilic sulfur center in sultones to prepare a variety of mono-, di-, tri-, and tetrasulfonyl fluorides. Tetrafluoroethane-β-sultone was reacted with polyfluoroalkyl alcohols to yield new polyfluoroalkyldifluoro(fluorosulfonyl)-acetates and di(polyfluoroalkyl) esters of difluoro(sulfonyl)acetic acid, e.g., $R_fOM + \overline{OCF_2CF_2SO_2} \rightarrow R_fOC(O)CF_2SO_2F$ where $R_f = CF_3CH_2$, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$, $C_7F_{15}CH_2$, $CF_3(CH_3)CH$, $(CF_3)_2CH$, $(CF_3)_2C(CH_3)$ and $CH_2(CF_3)_2CH_2$. By changing the stoichiometry to 2 moles alcohol/1 mole sultone, diesters, $R_fOC(O)CF_2SO_2OR_f$, were synthesized. In addition, alkylpoly[(fluorosulfonyl)-difluoroacetates] were obtained, e.g., $RCH_n(CH_2OH)_{3-n} + (3-n)\overline{OCF_2CF_2SO_2} \rightarrow RCH_n(CH_2OC(O)CF_2SO_2F)_{3-n}$ where $R = CH_3$, $n = 0$; O_2N, 0; $OC(O)CF_2SO_2F$, 2; $CH_2OC(O)CF_2SO_2F$, 0. The new mono- and diesters are all colorless, slightly volatile or involatile liquids at 25 °C. Each has high hydrolytic stability.[26]

Electron diffraction structure determinations were carried out in cooperation with Prof. H. Oberhammer of Tübingen. In this instance, two cyclic systems, $\overline{CF_2SF_4CF_2SF_4}$ and $\overline{CF_2CF_2CF_2CF_2SF_4}$, have been studied. Regardless of whether the compound is cyclic or acyclic, the S-C bond length is a function of the oxidation state of the sulfur -- the lower the oxidation state of sulfur, the shorter and, thus, stronger the bond. The $S-F_{ax}$ bond lengths are longer by 0.036 Å than the equatorial bonds and are slightly longer than in SF_6.[10,16]

E. Derivatives of sulfur hexafluoride resulting from oxidative addition-displacement reactions of trifluoromethylimidosulfites with chlorine fluoride. Some reactions of CF_3SF_4Cl.

The high kinetic stability of sulfur hexafluoride has caused it to be employed only rarely as a precursor to sulfur(VI)-containing compounds. Because of the inertness of the formal parent molecule, the search for alternate routes to mono, di and more highly substituted sulfur hexafluoride derivatives has continued to attract the attention of chemists with goals of synthesizing compounds of equivalent thermal and hydrolytic stability but, e.g., with higher boiling points or improved dielectric properties.

Earlier in these laboratories, a powerful route to the synthesis of N,N-dichloroperfluoroalkylamines and N,N-dichloroperfluoroalkylamides, R_fNCl_2 and $R_fC(O)NCl_2$, was discovered when the appropriate imidosulfurous difluorides were reacted with chlorine fluoride, e.g., $R_fN{=}SF_2$ ($R_fC(O)N{=}SF_2$) + excess ClF $\rightarrow R_fNCl_2$ ($R_fC(O)NCl_2$) + SF_4. In an attempt to determine the effect that less electronegative substituents on sulfur (other than fluorine) would have on the products formed when $R_fN{=}SX_2$ ($X \neq F$) was reacted with chlorine fluoride, a variety of bis(polyfluoroalkyl)(trifluoromethyl)imidosulfites were synthesized. Surprisingly, oxidative addition reactions between chlorine fluoride and trifluoromethylimidosulfites, $CF_3N{=}S(OR_f)_2$ [$R_f = CF_3CH_2$, $CF_3CF_2CH_2$, and $CF_3CF_2CF_2CH_2$], result in the formation of both the cis and trans tetrafluoro-bis(polyfluoroalkoxy)sulfur isomers, $F_4S(OR_f)_2$. The isomers are separated easily, with the trans form predominating. The trifluoromethylimidosulfites,

$CF_3N{=}S(OR_f)_2$ [R_f = CF_3CH_2, $CF_3CF_2CH_2$, $CF_3CF_2CF_2CH_2$, $(CF_3)_2C(CH_3)$, $CF_3C(CH_3)_2$ and $(CF_3)_2CH$], and $CF_3N{=}\overline{SOCH_2(CF_2)_2CH_2O}$, were prepared from the reaction of the lithium salts of the polyfluoroalkyl alcohols and trifluoromethylimidosulfurous difluoride. Reactions of ClF with $(CF_3CH_2O)_2S{=}NC(O)OCH_2CF_3$ also resulted in cis and trans-$F_4S(OCH_2CF_3)_2$. The reaction of ethylene glycol with trifluoromethylimidosulfurous difluoride resulted in the imidosulfite, $CF_3N{=}\overline{SOCH_2CH_2O}$, when NaF was used as a base.[20,17]

trans-Chlorotetrafluoro(trifluoromethyl)sulfur(VI), CF_3SF_4Cl, readily underwent reductive defluorination to sulfur(IV)-containing compounds when it was reacted with nitrogen- or oxygen-containing nucleophiles. Thus, $CF_3S(NR_2)_2Cl$ resulted from a variety of nitrogen bases, such as R_2NH = piperidine, 2,6-dimethylpiperidine, 2,2,6,6-tetramethylpiperidine, morpholine, 3,5-dimethylmorpholine, and N,N'-dimethylethenediamine. With alcohols, $CF_3S(OR_f)_2Cl$ was formed where R_fOH = 2,2,2-trifluoroethanol and 1,1,1-trifluoro-2-propanol. Due to the low stability of all of these compounds, complete characterization was difficult.[20]

F. Syntheses and structural characteristics of new highly fluorinated 1,3,2,4-di(t-butyl)diazaphosphetidines

In an attempt to learn more about the effects of introducing nonsterically demanding, as well as bulky, strongly electron-withdrawing substituents at phosphorus(III) in cis-$Cl\overline{PN(t\text{-}C_4H_9)P(Cl)}N(t\text{-}C_4H_9)$ (A) on the formation, stability, and relative amounts of cis and trans isomers, metathetical reactions with a variety of nucleophiles were attempted. A series of lithium salts of polyfluorinated alcohols were reacted with cis-A to form the polyfluoroalkoxy derivatives. The acyclic derivatives, i.e., R_fO = CF_3CH_2O, $CF_3CF_2CH_2O$, $CF_3CF_2CF_2CH_2O$, gave the trans isomer as the major stable product. However, the cis isomer is the major stable product formed between A and CF_3CH_2OH and $CF_3CF_2CF_2CH_2OH$ in the presence of triethylamine. The trans isomer also was the sole product with hexamethyldisilizane. However, when R_fO = C_6F_5O [24] or $(CF_3)_2CHO$, the cis isomer was the more stable conformer. Silver trifluoroacetate reacted with A resulting in the trans isomer as the major product that on standing at 25 °C underwent Arbuzov rearrangement to the trifluoroacetyl derivative, and phosphorus was, of course, oxidized to P(V). Reactions with lithiated polyfluorinated diols, $LiOCH_2(CF_2)_{2,3}CH_2OLi$, produced the polyfluorobisalkoxy-bridged diazaphosphetidines.[25]

G. Phosphorus(V) acids, acid phosphates, hypochlorites and peroxides and their precursors

Some new routes to the previously known acids $(R_f)_2P(O)OH$ and $R_fP(O)(OH)_2$ (R_f = CF_3, n-C_4F_9) as well as to the new acids $(C_2F_5)_2P(O)OH$ and $C_2F_5P(O)(OH)_2$ were found. In addition, several mixed chloro(perfluoroalkyl)phosphorus(III) and -(V) compounds have been synthesized as reaction precursors, including $(C_2F_5)_2PCl_3$, $C_2F_5PCl_4$, $(C_2F_5)_2PCl$, $C_2F_5PCl_2$, $(C_2F_5)_2P(O)Cl$, and $C_2F_5P(O)Cl_2$. Under certain conditions, when chlorophosphines were oxidized with an excess of NO_2, acid anhydrides resulted, e.g., $(C_2F_5)_2P(O)OP(O)(C_2F_5)_2$ and c-$(C_2F_5PO_2)_3$.[13]

The new dibasic acid phosphates, $R_fOP(O)(OH)_2$ (R_f = $(CF_3)_2CH$ and $CF_3(CH_3)CH$) and monobasic acid phosphates, $(R_fO)_2P(O)OH$ (R_f = $CF_3(CH_3)CH$, $(CF_3)_2CH$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$), as well as new routes to $CF_3CH_2OP(O)(OH)_2$, and $(CF_3CH_2O)_2P(O)OH$ and $[H(CF_2)_4CH_2O]_2P(O)OH$ were found. When heated in the

presence of water at 80 - 100 °C, $(R_fO)_2P(O)OH$ was hydrolyzed to $R_fOP(O)(OH)_2$ which was converted to H_3PO_4 at higher temperatures. The dibasic acid phosphates $R_fOP(O)(OH)_2$ (R_f = $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$) underwent dehydration to form $[R_fOP(O)(OH)]_2O$. Additionally, the chloro precursors to these acids have been synthesized, including the (polyfluoroalkyl)dichlorophosphinites, R_fOPCl_2 (R_f = CF_3CH_2, $CF_3(CH_3)CH$, $(CF_3)_2CH$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$), and bis(polyfluoroalkyl)chlorophosphonites, $(R_fO)_2PCl$ (R_f = CF_3CH_2, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$). If dinitrogen tetraoxide was used as an oxidant, the former were converted to $R_fOP(O)Cl_2$ and the latter to $(R_fO)_2P(O)Cl$. Lithium polyfluoroalkoxides with PCl_3 gave tris(polyfluoroalkyl)phosphites, $(R_fO)_3P$ (R_f = $CF_3(CH_3)CH$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$, CF_3CH_2, and $(CF_3)_2CH$), which were oxidized to $(R_fO)_3PO$ phosphates with N_2O_4. In some cases, $(R_fO)_2PCl$ (R_f = $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$) gave tetrakis(polyfluoroalkyl) diphosphates, $(R_fO)_2P(O)OP(O)(OR_f)_2$, and $CF_3CH_2OPCl_2$ gave $CF_3CH_2OP(O)(\mu\text{-}O)_2P(O)OCH_2CF_3$. The $(R_fO)_3P$ phosphites (R_f = CF_3CH_2, $CF_3(CH_3)CH$, $(CF_3)_2CH_3C$, $CF_3(CH_3)_2C$) underwent Arbuzov rearrangements with Cl_2 to form $(R_fO)_2P(O)Cl$. Hydrogen chloride converted $[CF_3(CH_3)_2CO]_3P$ to $[CF_3(CH_3)_2CO]_2P(O)H$, which with chlorine formed $[CF_3(CH_3)_2CO]_2P(O)Cl$.[15]

Tetrabasic 2,2,3,3-tetrafluoro-1,4-butanediyl bis(phosphate) and 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediyl bis(phosphate), $(HO)_2P(O)OCH_2(CF_2)_nCH_2OP(O)(OH)_2$ (n = 2, 4), and monobasic 5,5,6,6-tetrafluoro-2-hydroxy-1,3,2-dioxaphosphepane 2-oxide, $HO\overline{P(O)OCH_2CF_2CF_2CH_2O}$ were prepared by controlled hydrolysis of the appropriate bis(phosphorodichloridates) and 2-chloro-5,5,6,6-tetrafluoro-1,3,2-dioxaphosphepane 2-oxide, i.e., $Cl_2P(O)OCH_2(CF_2)_nCH_2OP(O)Cl_2$ (n = 2, 4) and $Cl\overline{P(O)OCH_2CF_2CF_2CH_2O}$. The latter compounds were obtained by the dinitrogen tetraoxide oxidation of $Cl_2POCH_2(CF_2)_nCH_2OPCl_2$ (n = 2, 4) and $Cl\overline{POCH_2CF_2CF_2CH_2O}$ which were synthesized from the reactions of PCl_3 with $HOCH_2(CF_2)_nCH_2OH$ (n = 2, 4) and $HOCH_2(CF_2)_2CH_2OH$, respectively. On heating at 95 °C in the presence of excess water, $HO\overline{P(O)OCH_2CF_2CF_2CH_2O}$ was converted to H_3PO_4 and the parent diol. The tetrabasic bis(phosphates) hydrolyzed at 175-200 °C to form H_3PO_4 and the respective diols.[18]

The new compounds, bis(perfluoroalkyl)phosphinyl hypochlorites, $(CF_3)_2P(O)OCl$, $(C_2F_5)_2P(O)OCl$ and $(C_4F_9)_2P(O)OCl$ were readily obtained by the reaction of the respective phosphinic acid, $(R_f)_2P(O)OH$, with chlorine fluoride at -78 °C. Each hypochlorite decomposed on warming to 25 °C to form chlorine and a new class of peroxides, $(CF_3)_2P(O)OOP(O)(CF_3)_2$, $(C_2F_5)_2P(O)OOP(O)(C_2F_5)_2$ and $(C_4F_9)_2P(O)OOP(O)(C_4F_9)_2$, which were stable for extended periods in Pyrex glass at 25 °C. Strong vibrational bands in the Raman spectra at ~ 750 cm^{-1} were assigned to ν_{O-O}.

H. Carbonyl fluoride as a novel fluorinating agent

A patent on the utilization of carbonyl fluoride as a mild fluorinating agent was filed by the Research Corporation but was subsequently rejected by the U. S. Patent Office. We continue to be interested in this method of introducing fluorine into metal and nonmetal compounds. The following points can be made with respect to its capabilities as a fluorinating agent.[2]

1. very effective as a nonoxidative reagent at $T \leq 150\ ^{\circ}C$ and without catalyst with metal oxides, e.g., GeO_2, SnO_2, Bi_2O_3, MoO_3, WO_3, Sb_2O_3, SeO_2, TeO_2, TiO_2, MnO_2, UO_3, ThO_2, HgO (yellow), VOF_3; with nonmetal oxides, e.g., SO_3, P_4O_{10}, SO_2, SOF_2, B_2O_3, Φ_3PO, $\Phi_3CH(CH_3)_2NH$, $(RO)_2P(O)H$. CO_2 is the other product.

2. oxidative fluorination at $25\ ^{\circ}C$ with R_3P, $(RO)_3P$, $\Phi PCH_2CH_2P\Phi_2$, $\Phi_2PCH_2CH_2As\Phi_2$. CO is the other product.

II. List of Publications

1. Scott A. Kinkead and Jean'ne M. Shreeve, "Regiospecific Addition of Trifluoramine Oxide to Trifluorovinyl Olefins," Inorganic Chemistry, 23, 3109 (1984).

2. O. D. Gupta and Jean'ne M. Shreeve, "Carbonyl Fluoride - A Versatile and Inexpensive Fluorinating Reagent," J.C.S. Chemical Communications, 416 (1984).

3. Helen M. Marsden and Jean'ne M. Shreeve, "The Syntheses of Heptafluoronitrosocyclobutane and Nonafluoronitrosocyclopentane and Their Reactions with Tetrafluoroethene, 1,3-Hexafluorobutadiene and Tetrafluorohydrazine," Inorganic Chemistry, 23, 3654 (1984).

4. Ramesh C. Kumar, Scott A. Kinkead, and Jean'ne M. Shreeve, "On the Reactions of Bis(2,2,2-Trifluoroethyl) Sulfite, Bis(hexafluoroisopropyl) Sulfite and Diethyl Sulfite with Chlorine Monofluoride - Evidence of Arbuzov Rearrangement," Inorganic Chemistry, 23, 3112 (1984).

5. Scott A. Kinkead and Jean'ne M. Shreeve, "Free Radical Decomposition of Trifluoramine Oxide: A Facile *In Situ* Source of Nitrosyl Fluoride," Inorganic Chemistry, 23, 4174 (1984).

6. Scott A. Kinkead, Ramesh C. Kumar and Jean'ne M. Shreeve, "Reactions of Polyfluoroalkyl Fluorosulfates with Nucleophiles: An Unusual Substitution at the Sulfur-Fluorine Bond," Journal of the American Chemical Society, 107, 7496 (1985).

7. Helen M. Marsden and Jean'ne M. Shreeve, "Perfluorocyclicalkyl(aryl) Diazenes from Heptafluoronitrosocyclobutane and Nonafluoronitrosocyclopentane," Journal of Fluorine Chemistry, 27, 275 (1985).

8. Håkon Hope, Clara Brink Shoemaker, David P. Shoemaker, Helen M. Marsden, and Jean'ne M. Shreeve, "Synthesis and Structure Determination of 3,3,4,4-Tetrafluoro-N-methyl-2-(cis,s-trans-methyl-NNO-azoxy)-s-cis-1-cyclobutene-1-amine," Journal of Organic Chemistry, 50, 1136 (1985).

9. Helen M. Marsden, Heinz Oberhammer, and Jean'ne M. Shreeve, "The Gas Phase Structure of Perfluoronitrosocyclobutane," Inorganic Chemistry, 24, 4756 (1985).

10. Krishna D. Gupta, Rüdiger Mews, Alfred Waterfeld, Jean'ne M. Shreeve and Heinz Oberhammer, "The Gas Phase Structures of Bis(Pentafluorothio)-difluoromethane and Tetrafluoro-1,3-dithietane Octafluoride," Inorganic Chemistry, 25, 275 (1986).

11. Ting-ji Huang and Jean'ne M. Shreeve, "Syntheses and Reactions of Polyfluoroalkyl Fluorosulfates," Inorganic Chemistry, 25, 496 (1986).

12. Wan Ahmad Kamil, Fritz Haspel-Hentrich, and Jean'ne M. Shreeve, "Synthesis and Reactions of Substituted Alkyl Trifluoromethyl Ethers," Inorganic Chemistry, 25, 376 (1986).

13. Tariq Mahmood and Jean'ne M. Shreeve, "Some New Perfluoroalkylphosphonic and Bis(perfluoroalkyl)phosphinic Acids and Their Precursors," Inorganic Chemistry, 25, 3128 (1986).

14. Jo Ann M. Canich, Megan E. Lerchen, Gary L. Gard and Jean'ne M. Shreeve, "Oxidative Addition/Addition Reactions of F-*tert*-Butyl Hypochlorite with Perfluoromono- or Perfluorodiiodoalkanes, Pentafluoroiodobenzene and Hexafluorobenzene," Inorganic Chemistry 25, 3030 (1986).

15. Tariq Mahmood and Jean'ne M. Shreeve, "Polyfluoroalkyl Dibasic Acid Phosphates. Bis(Polyfluoroalkyl) Monobasic Acid Phosphates and Their Precursors," Inorganic Chemistry, 25, 3830 (1986).

16. Krishna D. Gupta, Jean'ne M. Shreeve and Heinz Oberhammer, "The Gas Phase Structure of Dodecafluorooctahydrothiophene," Journal of Molecular Structure, 147, 363 (1986).

17. Helen M. Marsden and Jean'ne M. Shreeve, "*cis* and *trans*-Derivatives of Sulfur Hexafluoride Resulting from Oxidative Addition-Displacement Reactions of Trifluoromethylimidosulfite with Chlorine Fluoride," Inorganic Chemistry, 25, 4021 (1986).

18. Tariq Mahmood and Jean'ne M. Shreeve, "Polyfluoroalkanediyl Bis(phosphates).5,5,6,6-Tetrafluoro-2-hydroxy-1,3,2-dioxaphosphepane 2-oxide and Their Precursors," Inorganic Chemistry, 25, 4081 (1986).

19. Robin J. Terjeson, Roger M. Sheets, Gary L. Gard, Krishna D. Gupta and Jean'ne M. Shreeve, "Reactions of Trifluoromethyl Hypochlorite," Revue de Chimie Minerale, 23, 1 (1986).

21. Helen M. Marsden and Jean'ne M. Shreeve, "The Syntheses of Difluoroamino(difluoro)acetonitrile, *syn*-Fluoro(fluoroimino)acetonitrile, *syn*-3,3,3-Trifluoro-2-(fluoroimino)propanenitrile, and Their Reactions with Chlorine Fluoride. The Syntheses of Some New Perfluorinated Diazines," Inorganic Chemistry, 26, 169 (1987).

20. Krishna D. Gupta and Jean'ne M. Shreeve, "Some New Highly Substituted Trifluoromethyl Sulfuranes," Journal of Fluorine Chemistry, 34, 453 (1986).

22. Tariq Mahmood and Jean'ne M. Shreeve, "Bis(perfluoroalkyl)phosphinyl Hypochlorites and Dioxybis[bis(perfluoroalkyl)phosphine oxides]," Inorganic Chemistry, 26, 0000 (1987).

23. Earnest Obed John and Jean'ne M. Shreeve. "Some Fluorinated Heterocyclic and Acyclic Derivatives of Chlorocarbonylsulfenyl Chloride." Journal of Fluorine Chemistry, 35, 0000 (1987).

24. Wan A. Kamil. Marcus R. Bond. and Jean'ne M. Shreeve. "The Synthesis and X-Ray Structure of cis-1,3-Di(t-butyl)-2,4-bis(pentafluorophenoxy)-1,3,2,4-diazadiphosphetidine." Inorganic Chemistry, 26, 0000 (1987).

25. Wan A. Kamil and Jean'ne M. Shreeve. "The Syntheses and Structural Characteristics of Some New Highly Fluorinated 1,3,2,4-Di(t-butyl)-diazaphosphetidines." Inorganic Chemistry, 26, 0000 (1987).

26. Ting-ji Huang. Zhi-Xia Dong and Jean'ne M. Shreeve, "Synthesis of Polyfluoroalkyl Esters of Difluoro(fluorosulfonyl)acetic Acid and Diesters of Sulfonyldifluoroacetic Acid." Inorganic Chemistry, 26, 0000 (1987).

27. Earnest Obed John and Jean'ne M. Shreeve, "Reactions of Difluoroamino-(difluoro)acetonitrile." Inorganic Chemistry, in progress.

28. Jerry Foropoulos. Jr., and Jean'ne M. Shreeve, "Reactions of Polycyano Compounds with Chlorine Fluoride," Inorganic Chemistry, in progress.

III. Personnel

Dr. Jean'ne M. Shreeve	PI
Dr. Jerry Foropoulos, Jr.	Postdoctoral
Dr. Henrik Juve	Research Associate
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Helen Marsden	Ph.D. candidate - completed
Kamil Ahmad	Ph.D. candidate - completed
Tariq Mahmood	Ph.D. candidate - completed
Earnest John	Ph.D. candidate
Xiongbing Xia	Ph.D. candidate
Zhi-Xia Dong	Research Associate

IV. Presentations

"Fluoronitrogen Compounds," 1983 and 1985 AFOSR/AFRPL Rocket Propulsion Research Meetings. March 1983 and 1985, Lancaster, CA.

"Some New Perfluorinated Diazines and Their Reactions," Centenary of the Discovery of Fluorine, August 1986, Paris, France.

"Fluorinated Rings and Things," Washington State University, November 1986, Pullman, WA.

"Inorganic Fluorine Chemistry," 191st National Meeting of the American Chemical Society, April 1986, New York, NY.

"Hypochlorites and Peroxides of Bis(perfluoroalkyl)phosphinic Acids." (with T. Mahmood) 191st National Meeting of the American Chemical Society, April 1986, New York, NY; and 41st Northwest Regional American Chemical Society Meeting, June 1986, Portland, OR.

"Synthesis and Reactions of Various Perfluoroalkoxy Derivatives of P-N Ring Systems," (with W. Kamil) 41st Northwest Regional American Chemical Society Meeting, June 1986, Portland, OR.

"Synthesis of New Fluorosulfonyl Systems and Their Derivatives," (with T. Huang, Z. Dong and G. Gard) Centenary of the Discovery of Fluorine, August 1986, Paris, France.

"New and Interesting F-tert-Butoxide Perfluoroalkyliodine(III) Complexes," (with G. Gard) 41st Northwest Regional American Chemical Society Meeting, June 1986, Portland, OR.

"Preparation and Reaction of Alkyldifluoro(fluorosulfonyl)acetates," (with T. Huang and Z. Dong) 41st Northwest Regional American Chemical Society Meeting, June 1986, Portland, OR.

"Fluorinated Sulfur and Nitrogen Compounds," Stauffer Chemical Co., March 1986, New York, NY.

"New Fluorinating Reagents," Allied-Signal, March 1986, Buffalo, NY.

"Reactions of $(R_f)_2SO$ and $(R_fO)_2SO$- or, Oh, What a Difference an Oxygen Makes," University of Wisconsin and University of Colorado, Spring 1985, EauClaire, WI, and Colorado Springs and Pueblo, CO.

"Carbonyl Fluoride - New Uses for an Old Friend," University of Wisconsin, Spring 1985, LaCrosse, WI.

"Carbonyl Fluoride Compared with Sulfinyl Fluoride as an Effective Fluorinating Reagent," University of Wisconsin, Spring 1985, Milwaukee, WI.

"Syntheses of Some New Fluorosulfur and Fluoronitrogen Compounds," Plenary Lecture, International Symposium on Fluorine Chemistry, August 1985, Berlin, GDR.

"Fluorinated Sulfur(VI) Compounds - Always Some Surprises," University of Houston and Texas A&M University, College Station, TX, Fall 1985.

"Preparation and Reactions of Polyfluoroalkyl Fluorosulfates," (with T. Huang) 40th Northwest Regional American Chemical Society Meeting, June 1985, Sun Valley, ID.

"Some New Reactions of Iminosulfur Difluorides," (with H. Marsden) 40th Northwest Regional American Chemical Society Meeting, June 1985, Sun Valley, ID.

"Nucleophilic Reactions of Alcohols and Amines with trans-chlorotetrafluoro(trifluoromethyl)sulfur(VI)," (with K. D. Gupta) 40th Northwest Regional American Chemical Society Meeting, June 1985, Sun Valley, ID.

"Reactions of Various Substituted Olefins with Trifluoromethyl Hypochlorite," (with W. Kamil) 40th Northwest Regional American Chemical Society Meeting, June 1985, Sun Valley, ID.

"Further Reactions of Carbonyl Fluoride," 40th Northwest Regional American Chemical Society Meeting, June 1985, Sun Valley, ID.

"Chemistry of Phosphorus Oxyacids," (with T. Mahmood) 40th Northwest Regional American Chemical Society Meeting, June 1985, Sun Valley, ID.

"Some New F-alkyl and Cyclic F-Alkyl Phosphorus(V) Acids and Their Precursors," (with T. Mahmood) 190th National American Chemical Society Meeting, Sept. 1985, Chicago, IL.

"Preparation and Reactions of Trifluoromethyliminosulfites," (with H. Marsden) 190th National American Chemical Society Meeting, Sept. 1985, Chicago, IL.

"Fluorinated Cyclic Nitroso Compounds as a Route to Fluorinated Oxazetidines, Oxazines, Difluoroamines, Nitro and Azoxy Compounds," (with H. M. Marsden) 39th Northwest Regional American Chemical Society Meeting, June 1984, Moscow, ID.

"Synthesis and Structure of 3,3,4,4-Tetrafluoro-N-methyl-2-(z-methylazoxy)-1-cyclobutene-1-amine," (with H. Hope, C. B. Shoemaker, D. P. Shoemaker, H. M. Marsden) 39th Northwest Regional American Chemical Society Meeting, June 1984, Moscow, ID.

"New Fluorosulfur Heterocycles (I) - Pentafluorosulfur Sultone and Derivatives," (with J. Canich, M. M. Ludvig, and G. L. Gard) 39th Northwest Regional American Chemical Society Meeting, June 1984, Moscow, ID.

"Preparation and Properties of Polyfluoroalkyl Fluorosulfates," (with S. A. Kinkead) 39th Northwest Regional American Chemical Society Meeting, June 1984, Moscow, ID.

"Nucleophilic Substitution in Fluorosulfates," (with R. C. Kumar and S. A. Kinkead) 39th Northwest Regional American Chemical Society Meeting, June 1984, Moscow, ID.

"Pentafluorosulfur Sultone and Some Derivatives," (with J. M. Canich, M. M. Ludvig and G. L. Gard) 188th National American Chemical Society Meeting, August 1984, Philadelphia, PA.

"The Reaction of Polyfluoroalkyl Fluorosulfates with Hard and Soft Nucleophiles," (with S. A. Kinkead and R. C. Kumar) 188th National American Chemical Society Meeting, August 1984, Philadelphia, PA.

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